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Materials and Manufacturing of Electrochemical Cells for Reduction of CO_2 into Liquid Fuels

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Co-electrolysis of CO_2 and H_2O are conventionally performed with solid oxide electrolyzer cells at temperatures between 750 - 1000 °C. Electrolysis performed at these high temperatures will give syngas (CO and H_2) as the product. Syngas can then be further converted into synthetic fuels (like hydrocarbons or alcohols) at lower temperatures. [1] Co-electrolysis at temperatures of 200 - 300 °C, where hydrocarbons are stable, might have the advantage that CO_2 and H_2O can be converted into liquid synthetic fuels directly in the cell. Operating at temperatures above 200 °C and at elevated pressures may make it possible to use non precious metals as electrocatalysts. Both new electrolyte and electrode materials are needed to build up electrochemical cells for this purpose.

A number of different materials have shown promising proton conductivities in the desired temperature range (200 - 300 °C), where solid acids are one example. CsH_2PO_4 is the most investigated solid acid and shows high proton conductivity (10^{-2} S cm^{-1}), but only in a narrow temperature range. High temperatures or low partial pressure of water will lead to dehydration of the material. [2] Copper is a possible electrocatalyst for reduction of CO_2 into hydrocarbons. [3] Generally precious metal oxides, like IrO_2 and RuO_2, are used for water splitting at low temperatures. NiO_x is another non precious material that possibly can be used for oxygen evolution, if corrosion can be avoided in the acid environment.

Proton conductivity measurements of $BaHPO_4$, CsH_2PO_4 and a composite of $BaHPO_4$ and CsH_2PO_4 (50:50 wt%) have been performed at various temperatures up to 250 °C (300 °C for $BaHPO_4$), various humidity's (up to 0.30 bar H_2O) and in a variety of atmospheres. The conductivity was measured with electrochemical impedance spectroscopy on circular disc with a thickness of ~1 mm. Figure 1 and 2 show measured conductivity's and long term stability of the investigated electrolytes.

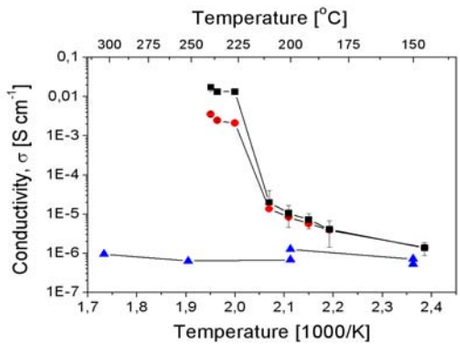

Figure 1. Arrhenius plot of CsH_2PO_4 (■), $BaHPO_4$ (▲) and a composite of CsH_2PO_4 and $BaHPO_4$ [50:50 wt%] (●). Atmosphere: 7 % H_2, 73 % N_2 and 20 % H_2O

CsH_2PO_4 showed stable conductivity values (~20 mS cm^{-1} at 240 °C) in good agreement with literature. It can also be seen in figure 2 that it is possible to regain the conductivity after treatment at temperatures where it is non stable, i.e. dehydrating. Powder x-ray diffraction measurements showed that even the crystal structure recovered, meaning that the material regenerates after some initial dehydration. The thermal stability of $BaHPO_4$ was seen to be higher than that of CsH_2PO_4 and also higher than that of the composite, but the conductivity is low. This can possibly be explained by the difference in valence of the cations (Cs^+, Ba^{2+}), the divalent barium will bond harder to the phosphate group and might hinder the rotation that causes the high conductivity in CsH_2PO_4. The conductivity of the composite lies in between the ones for the two single phased materials.

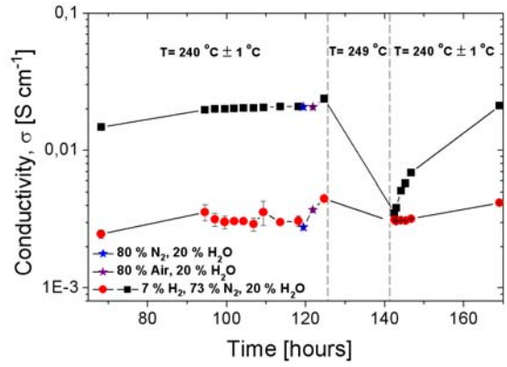

Figure 2. Measured conductivity of CsH_2PO_4 (■) and a composite of CsH_2PO_4 and $BaHPO_4$ [50:50 wt%] (●) as a function of time. p(H_2O)= 0.20 bar

Moreover, a number of electrodes have been manufactured using different procedures. Cu- and NiO-electrocatalysts have been infiltrated into electron conducting backbones. Slurries containing NiO and Cu have also been manufactured and deposited onto supporting substrates. Full cells are prepared by pressing the electrolyte and the electrodes together; this method is used due to the low thermal stability of the electrolyte. Figure 3 shows a micrograph of a pressed CsH_2PO_4 electrolyte after removal of electrodes.

Characterization and optimization of the electrodes is needed before full cells can be tested in order prove if liquid synthetic fuels can be produced as a one step process in electrochemical cells.

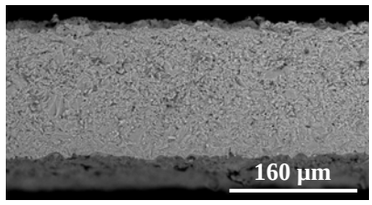

Figure 3. Micrograph showing a CsH_2PO_4 electrolyte with a thickness of 160 µm.

Acknowledgement
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